

TITLE OF THE INVENTION

METHOD FOR PRODUCING ALLYL COMPOUND

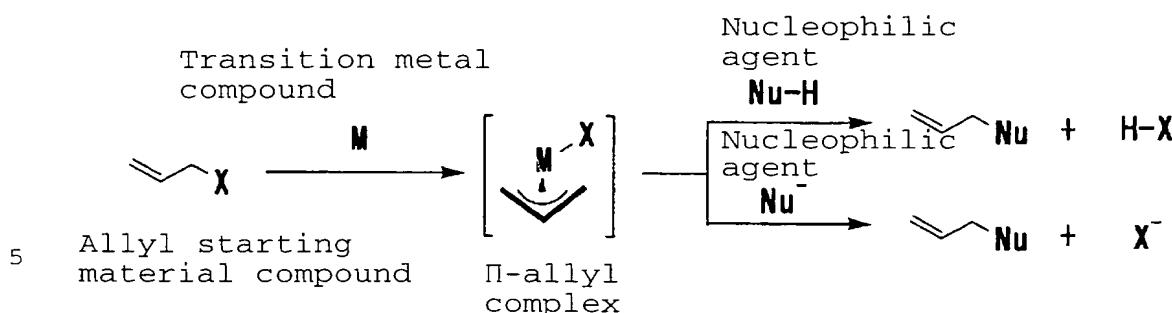
BACKGROUND OF THE INVENTION

5 FIELD OF THE INVENTION

The present invention relates to a method for producing a new allyl compound different from an allyl starting material compound by reacting the allyl starting material compound with an oxygen nucleophilic agent in
10 the presence of a catalyst.

PRIOR ARTS

Various kinds of new allyl compounds can be synthesized by carrying out a catalytic reaction using a transition metal compound and using an allyl compound as
15 a starting material. This reaction proceeds as illustrated in the following reaction formula, wherein an allyl starting material compound having an eliminating group X is π -coordinated and oxidatively added to a transition metal compound to form a π -allyl complex
20 having three carbons of the allyl part bonded to a metal and the terminal allyl carbon of the π -allyl complex is attacked by a nucleophilic agent expressed by Nu-H or Nu⁻.



The synthesizing reaction of an allyl compound is generally fully described in "Palladium Reagents and Catalysts -Innovations in Organic Synthesis-" published by John Wiley & Sons Company, and various products in a form of allylated nucleophilic agent can be obtained by electing a kind of a nucleophilic agent in the reaction. Among them, when the nucleophilic agent is an oxygen nucleophilic agent such as alcohols, phenols, or carboxylic acids, respective allyl alkyl ether, allyl phenyl ether or allyl carboxylate esters are synthesized, and they are considered to be one of basic reactions useful in synthetic chemistry.

However, as a reaction example of an allyl starting material compound and an oxygen nucleophilic agent, the case in which the oxygen nucleophilic agent is carboxylic acid anion, is generally well known, but there are not so many reaction examples with other oxygen nucleophilic agents due to their low reactivity.

25 For example, as described in "Organometallics, 1995, 14, p. 4585" illustrating a reaction example with phenols, a synthesis example of allyl phenyl ethers by a

palladium catalyst system having a triaryl type monodentate phosphite ligand such as triphenyl phosphite is well known, but its activity is not sufficient.

Also, reaction examples with alcohols are very limited due to low nucleophilic attacking property of alcohol oxygen. As a reaction example between molecules of alcohol oxygen and an allyl starting material compound, dehydration condensation reaction of an allyl alcohol by a catalyst system using a monodentate phosphite ligand of triphenyl phosphite or triethyl phosphite was reported in "Nihon Kagakukai Kouen Yokoushuu, 2001, Vol. 79th, No. 2, p. 1194" and "Nihon Gakujutsu Shinkoukai Souzou Kinou Kagaku Dai 116 Iinkai 2002, 6, Godou Bunkakai Shiryou p. 46", but in this reaction, a wide variety of synthesis can not be carried out since the allyl starting material compound and the oxygen nucleophilic agent are both allyl alcohols. Also, a reaction of alcohols with an allyl alcohol by a catalyst system comprising triphenylphosphite considered to have a highest activity was also reported, but its catalyst activity is still not high.

As an example of attacking a π -allyl complex by other alcohol oxygen, there are known some cyclizing reactions wherein the cyclization is carried out intramolecularly by attacking π -allyl terminal carbon with alcohol oxygen present at such a position as to form a 5-membered ring or a 6-membered ring in the reaction

process. For example, as described in "Tetrahedron Lett., 1995, 36, p. 5527", there is known a synthesis example of a morpholine derivative by a palladium catalyst system having triisopropyl phosphite as a monodentate phosphite ligand. Also, a synthesis example of a 5-membered cyclic product by a palladium catalyst system having a bidentate phosphite ligand having cyclic both terminals composed of a pentan-2,5-diyl group was reported in "J. Am. Chem. Soc., 1998, 120, p. 1732".

However, it is necessary for these reactions that an oxygen nucleophilic agent is present at such a position as to easily form a ring, and they are allylation reaction which can proceed only intramolecularly and which is a special system.

As mentioned above, although it is possible to produce ether compounds or ester compounds important in organic synthesis by their reaction of an allyl starting material compound and its different oxygen nucleophilic agent, a highly active catalyst system which can sufficiently react an oxygen nucleophilic agent having a low reactivity has not been developed, and therefore practical reaction examples are actually limited. Particularly, in the reaction with alcohols, it is impossible to sufficiently proceed the reaction unless a special environment such as the above-mentioned intramolecular cyclization reaction is provided. Therefore, it has been demanded to develop a new catalyst

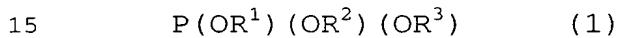
system which achieves a sufficiently high catalyst activity even in the reaction with such an oxygen nucleophilic agent as having a low reactivity.

The present invention has been made for solving the
5 above-mentioned problems. Thus, an object of the present invention is to provide a method for producing an allyl compound, which can efficiently produce various allyl compounds by using a new catalyst system achieving an especially high activity to such an oxygen nucleophilic
10 agent as having a low reactivity in the reaction of an allyl starting material compound and an oxygen nucleophilic agent, and to provide an ether compound and an ester compound produced thereby.

The present inventors have intensively studied to
15 develop a catalyst system capable of efficiently proceeding a reaction among molecules of various allyl starting material compounds and their different oxygen nucleophilic agents, and have discovered that a catalyst system comprising a trialkyl type monodentate coordinated phosphite compound and a transition metal compound of Group 8 to Group 10 of the Periodic Table achieves an unexpectedly very high activity as compared with a conventional catalyst system of monodentate phosphine or bidentate phosphine and a catalyst system of triphenyl
20 phosphite known as a prior art. The present invention has been accomplished on the basis of this discovery.
25

SUMMARY OF THE INVENTION

That is, the essential feature of the present invention resides in a method for producing a new allyl compound having a compositional formula different from 5 that of an allyl starting material compound, which comprises reacting the allyl starting material compound with an oxygen nucleophilic agent having a structure different from that of the allyl starting material compound in the presence of a catalyst containing at 10 least one transition metal compound containing a transition metal selected from the group consisting of transition metals belonging to Group 8 to Group 10 of the Periodic Table and a monodentate phosphite compound having a structure of the following formula (1):



wherein R¹, R² and R³ are respectively independently an alkyl group which may have a substituent, carbon chains of R¹, R² and R³ may have at least one carbon-carbon double bond or triple bond, and at least two optional groups of R¹, R² and R³ may bond to each other to form at 20 least one cyclic structure.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

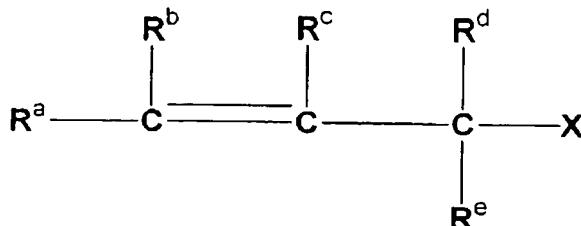
Hereinafter, the present invention is described in more details.

25 A method for producing an allyl compound in accordance with the present invention (hereinafter referred to as "production method of the present

invention") produces a new allyl compound having a compositional formula different from an allyl starting material compound by reacting the allyl starting material compound with an oxygen nucleophilic agent having a 5 structure different from that of the allyl starting material compound in the presence of a catalyst containing the following specific transition metal compound and the following monodentate coordinated phosphite compound having a specific structure.

10 First, the allyl starting material compound used in the production method of the present invention is explained hereinafter. The allyl starting material compound is not specially limited so long as it has an allyl group and an eliminating group in a molecule, but 15 has a total molecular weight of at most 1,500 (about at most 100 carbon atoms), and it is preferable that under reaction conditions, a part or all of the allyl starting material compound is soluble in a solvent, compatible with an oxygen nucleophilic agent, or meltable by melting 20 with heat. Among them, a preferable example is a compound having such a structure as expressed by the following formula (a) wherein an eliminating group expressed by X is bonded to an allyl group having a group expressed by R^a to R^e. The eliminating group means an 25 atom or an atom group which is bonded to carbon of a substrate structure (allyl structure in the present invention) as a matrix and is generally an electron

withdrawing group and is eliminated from the substrate molecule having an electron pair.



In the above formula (a), R^a to R^e are respectively
5 independently a hydrogen atom, a halogen atom, a hydroxy group, an amino group, a formyl group, a chain-like or cyclic alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an amide group, an acyl group or an acyloxy group (in the
10 present specification, the aryl group includes a heterocyclic compound forming an aromatic 6π electron cloud on the upper and lower parts of the ring). The above illustrated groups may further have a substituent. Examples of the substituent are not specially limited so
15 long as they do not affect adversely the reaction system, but preferable examples include a halogen atom, a hydroxy group, an amino group, a formyl group, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an amide group, an
20 acyl group or an acyloxy group.

Preferable examples of the above R^a to R^e include a hydrogen atom, a halogen atom, a hydroxy group, an amino group, a chain-like or cyclic alkyl group which may be

substituted with the above substituents, an aryl group which may be substituted with the above substituents, an alkoxy group which may be substituted with the above substituents, an aryloxy group which may be substituted with the above substituents, an alkylthio group, an arylthio group, an acyl group or an acyloxy group, and more preferable examples include a hydrogen atom, a halogen atom, a hydroxy group, an amino group, a chain-like or cyclic alkyl group which may be substituted with the above substituents, an aryl group which may be substituted with the above substituents, an alkoxy group, an arylalkoxy group, an aryloxy group, an alkylaryloxy group, an alkylthio group, an arylthio group, an acyl group or an acyloxy group.

The carbon number of R^a to R^e is generally at most 40, preferably at most 30, more preferably at most 20. When R^a to R^e is a group containing a carbon chain, the group may have at least one carbon-carbon double bond or triple bond in the carbon chain.

Among the above illustrated groups, particularly preferable R^a to R^e are respectively independently a hydrogen atom, a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group.

Also, a group adversely affecting the reaction system is a material poisoning a catalyst such as a group containing conjugated diene, a material oxidizing and decomposing a phosphite compound such as a group

containing peroxide or the like. Accordingly, in the present specification, a group "having no adverse affection on the reaction system" means to exclude these groups adversely affecting the reaction system.

5 On the other hand, examples of the eliminating group X include a halogen atom, a hydroxy group, a nitro group, an amino group expressed by R'_2N- , a sulfonyl group expressed by RSO_2- , a sulfonate group expressed by RSO_2O- , an acyloxy group expressed by $RC(=O)O-$, a carbonate group expressed by $R'OC(=O)O-$, a carbamate group expressed by $R'NHC(=O)O-$, a phosphate group expressed by $(R'O)_2P(=O)O-$, or an alkoxy group or an aryloxy group expressed by $RO-$. In the above formulae, R is a monovalent organic group and R' is a hydrogen atom
10 or a monovalent organic group. The kind of the organic group is not specially limited so long as it does not adversely affect the reaction system, but preferable examples include an alkyl group or an aryl group. When R is an organic group, its carbon number is generally from
15 1 to 40, preferably from 1 to 30, more preferably from 1 to 20. When the eliminating group X is a group containing a carbon chain, it may have at least one carbon-carbon double or triple bond in a carbon chain.

Among the above illustrated examples, X is
25 preferably an acyloxy group having a structure expressed by $-C(=O)O-$, a carbonate group, a carbamate group, a phosphate group having a structure expressed by $=P(=O)-$

or a sulfonate group having a structure expressed by $-S(=O)_2O-$, and particularly preferable examples include an acyloxy group and a carbonate group. Examples of the acyloxy group include a C₁-C₆ acyloxy group such as an acetoxy group, a propionyloxy group, a butyryloxy group or an isobutyryloxy group. Examples of the carbonate group include a C₁-C₆ alkylcarbonate group such as a methylcarbonate group, an ethylcarbonate group or a C₆-C₁₂ arylcarbonate group such as a phenylcarbonate group. A particularly preferable example of X is an acyloxy group, and most preferable example of X is an acetoxy group.

Among the above R^a to R^e and X, at least two optional groups may be bonded to each other to form at least one cyclic structure. However, when X is contained in a stable cyclic structure, it is not preferable since X is hardly eliminated. The number of cyclic structures is not specially limited, but is generally from 0 to 3, preferably from 0 to 2, particularly preferably from 0 or 1. Also, the number of atoms forming each ring is not specially limited, but is usually 3 to 10-membered ring, preferably 4 to 9-membered ring, particularly preferably 5 to 7-membered ring. When a plurality of rings are present, these rings may be partly commonly owned to form a condensed ring structure.

When at least two groups of R^a to R^e and X are bonded to form a cyclic structure, its carbon number is usually

0 to 40×p, preferably 0 to 30×p, more preferably 0 to 20×p, wherein p is a number of groups participating in the formation of the ring structure.

Examples of the allyl starting material compound
5 expressed by the above formula (a) include preferably halogenated allyls, allyl alcohols, allylamines, allyl sulfones, allyl sulfonates, allyl esters of carboxylic acids, allyl carbonates, allyl carbamates, allyl esters of phosphoric acid, allyl ethers, vinyl ethylene oxides,
10 and the like.

Examples of the halogenated allyls include allyl chloride, 2-butenyl bromide, 1-chloro-2-phenyl-2-pentene and the like.

Examples of the allyl alcohols include 2-butenyl
15 alcohol, 2,3-dimethyl-2-butenyl alcohol, 3-bromoallyl alcohol and the like.

Examples of the allylamines include allyldiethylamine, 3-methoxyallyldiphenylamine, triallylamine, 2-butenyldibenzylamine, and the like.

20 Examples of the allyl sulfones include allyl phenyl sulfone, methylallyl-p-tolylsulfone, 2-methyl-3-sulfolene, 1,3-diphenylallylmethylsulfone, and the like.

Example of the allyl sulfonates include allyl toluene-4-sulfonate, 3-thiophenmethanesulfonate, 4-
25 chloro-2-butenylmethanesulfonate, and the like.

Example of the allyl esters of carboxylic acid include allyl acetate, 2-hexenyl acetate, 2,4-hexadienyl

acetate, prenyl acetate, geranyl acetate, farnesyl acetate, cinnamyl acetate, rinaryl acetate, 3-butene-2-yl acetate, 2-cyclopentenyl acetate, 2-trimethylsilylmethyl-2-propenyl acetate, 2-methyl-2-cyclohexenyl acetate, 1-5 phenyl-1-butene-3-yl propionate, 1-cyclohexyl-2-butene butyrate, 4-cyclopenten-1,3-diol-1-acetate, 1,4-diacetoxy-2-butene, 3-acetoxy-4-hydroxy-1-butene, and the like.

Example of the allyl carbonates include allylmethyl carbonate, 10 4-acetoxy-2-butenylethyl carbonate, nerylmethyl carbonate and the like.

Examples of the allyl carbamates include allyl-N-(4-fluorophenyl)carbamate, 2-butenyl-N-methyl carbamate, furfuryl-N-(2-methoxydiphenyl)carbamate and the like.

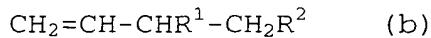
15 Examples of the allylesters of phosphoric acid include allyldimethyl phosphate, 3-methyl-2-butenyldiphenyl phosphate, methylethylfurfuryl phosphate and the like.

Examples of the allyl ethers include allyl ethyl ether, allyl phenyl ether, 2,3-diphenylallylisopropyl ether, 2-butenyl-4-fluorophenyl ether and the like.

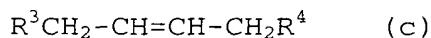
Examples of the phenylethylene oxides include butadiene monoxide, cyclopentadiene monoxide, 1,3-cyclohexadiene monoxide and the like.

25 Particularly preferable examples of the allyl starting material compound include a mixture of at least two compounds selected from the group consisting of 3,4-

disubstituted 1-butene expressed by the following formula (b), 1,4-disubstituted 2-butene expressed by the following formula (c) and their compounds.



In the above formula (b), R¹ and R² are respectively independently an acetoxy group or a hydroxyl group, at least one of which is an acetoxy group. Examples of the 3,4-disubstituted 1-butene expressed by the above formula (b) include 3,4-diacetoxy-1-butene, 3-acetoxy-4-hydroxy-1-butene, 4-acetoxy-3-hydroxy-1-butene and the like.



In the formula (c), R³ and R⁴ are respectively independently an acetoxy group or a hydroxyl group, at least one of which is an acetoxy group. Examples of the 1,4-disubstituted 2-butene expressed by the above formula (c) include 1,4-diacetoxy-2-butene, 1-acetoxy-4-hydroxy-2-butene and the like.

Next, the oxygen nucleophilic agent used in the production method of the present invention is explained hereinafter. Generally, a nucleophilic agent is a reactive material having a non-covalent electron pair, which is basic and has a tendency of attacking a carbon nucleus, but in the present invention, every reactive material having a non-covalent electron pair on an oxygen atom and having a tendency of attacking an allyl-terminated carbon nucleus of n-allyl complex with the electron pair is used as the oxygen nucleophilic agent.

Examples of the oxygen nucleophilic agent usable in the present invention include a proton adduct compound expressed by AO-H containing a nucleophilic oxygen atom, an anion expressed by AO⁻ which is a deprotonated material, or a compound which can be an anion in the reaction system. In the above formula, A is a hydrogen atom or an organic group. The organic group is a material having a carbon atom, a nitrogen atom, a phosphorus atom or a sulfur atom bonded to the nucleophilic oxygen atom, which becomes a liquid in the reaction system and does not adversely affect the reaction system. The carbon number of the organic group is generally in a range of from 1 to 40 so that it can be easily soluble in the reaction system, and the carbon number is preferably from 1 to 30, more preferably from 1 to 20.

Examples of the organic group bonded to the nucleophilic oxygen atom by way of a carbon atom include an unsubstituted or substituted chain-like or cyclic alkyl group, an unsubstituted or substituted aryl group or an acyl group.

Examples of the organic group bonded to the nucleophilic oxygen atom by way of a nitrogen atom include an unsubstituted or substituted amino group or a group having a C=N bond.

Examples of the organic group bonded to the nucleophilic oxygen atom by way of a phosphorus atom

include an unsubstituted or substituted phosphonate group, an unsubstituted or substituted phosphinate group or an unsubstituted or substituted phosphinoyl group.

Examples of the organic group bonded to the
5 nucleophilic oxygen atom by way of a sulfur atom include an unsubstituted or substituted sulfonyl group.

Substituents of the above illustrated groups are not specially limited so long as they are an organic group and do not adversely affect the reaction system, and
10 preferable examples include a chain-like or cyclic alkyl group, an aryl group, an alkoxy group, an arylalkoxy group, an aryloxy group, an alkylaryloxy group, an alkylthio group, an arylthio group, an acyl group or an acyloxy group. When the above illustrated groups have
15 these substituents, the total carbon number including substituents should be within the above-mentioned range.

However, even when an oxygen nucleophilic agent is within the above-mentioned definition, it is necessary to exclude such an oxygen nucleophilic agent as to be the
20 same as substituent (X or its anion X⁻ in the above formula (a)) or its proton adduct (X-H), which is eliminated from an allyl starting material compound depending on the reaction, since it provides such a state as not proceeding the reaction apparently or such a state
25 as producing an isomerized material only of the allyl starting material compound as a product. Also, it is necessary to exclude such an oxygen nucleophilic agent as

to be completely the same as the allyl starting material compound, and for example, when the oxygen nucleophilic agent and the allyl starting material compound are both allyl alcohols, its product is limited to a diallyl ether
5 having a structure obtained by simple dehydration condensation of the starting material, as previously described with regard to the prior art. Such an oxygen nucleophilic agent should be excluded since it is less important in respect of carrying out a wide variety of
10 synthesis.

Among the above explained oxygen nucleophilic agents, a preferable oxygen nucleophilic agent is a material having a total molecular weight of at most 400 (about at most 30 carbon atoms), a part or all of which
15 is soluble in a solvent, compatible with an allyl starting material compound, or meltable by melting with heat.

Examples of an oxygen nucleophilic agent in a proton adduct form (AO-H) are illustrated below. When A is a
20 hydrogen atom, it is water.

When A is an organic group having a nucleophilic oxygen bonded a carbon atom, their examples include hydroxy compounds, carboxylic acids, thiocarboxylic acids or selenocarboxylic acids.

25 Examples of the hydroxy compounds include alcohols such as methanol, ethanol, n-propanol, n-butanol, sec-butanol, t-butanol, allyl alcohol, 2-ethylhexyl alcohol,

4-chloro-1-butanol, benzyl alcohol, cyclohexanol, ethylene glycol, 1,3-propanediol and 1,4-butanediol; and phenols such as phenol, p-methoxyphenol, 2,4-dimethylphenol, 1-naphthol, 2-naphthol, 3,6-di-t-butyl-2-naphthol, 2-pyridinol or 2-bromo-4-pyridinol.

Examples of the carboxylic acids include aliphatic carboxylic acids such as acetic acid, propionic acid, butyric acid, chloroacetic acid, oxalic acid or adipic acid; and aromatic carboxylic acids such as benzoic acid, naphthalene-2-carboxylic acid, m-cyanobenzoic acid or o-toluic acid.

Examples of the thiocarboxylic acids include a compound expressed by $\text{CH}_3\text{C}(=\text{S})-\text{OH}$ or a compound expressed by $\text{PhC}(=\text{S})-\text{OH}$.

Examples of the selenocarboxylic acids include a compound expressed by $\text{CH}_3\text{C}(\text{C}=\text{Se})-\text{OH}$ or a compound expressed by $\text{PhC}(=\text{Se})-\text{OH}$. In the present specification, Ph means a phenyl group.

When A is an organic group wherein a nucleophilic oxygen and a nitrogen atom are bonded to each other, its examples include hydroxyamines such as N,N-diethylhydroxyamine, N,N-dibenzylhydroxyamine or the like; oximes such as acetone oxime, benzophenone oxime, cyclopentanone oxime or the like; and t-butyl-N-hydroxycarbamate, N-hydroxymaleimide, N-hydroxy succinimide, 1-hydroxybenzotriazole, and the like.

When A is an organic group wherein a nucleophilic

oxygen and a phosphorus atom are bonded to each other, its examples include phosphinic acids, phosphonic acid esters, phosphoric acid esters, and the like.

Examples of the phosphinic acids include
5 dimethylphosphinic acid, diphenylphosphinic acid or the like; examples of the phosphonic acid esters include ethyl phosphonic acid, propyl phosphonic acid monophenyl ester or the like; and examples of the phosphoric acid esters include diphenyl phosphate, dimethyl phosphate or
10 the like.

When A is an organic group wherein a nucleophilic oxygen and a sulfur atom are bonded to each other, its examples include sulfonic acids such as p-toluenesulfonic acid, methanesulfonic acid, ethanesulfonic acid or the
15 like; and sulfuric acid monoesters such as sulfuric acid monophenylester, sulfuric acid monoocystylester or the like.

All of the above illustrated examples are shown in a proton adduct form, but each of the above illustrated
20 compounds includes a deprotonated product or a compound convertible to its deprotonated product in the reaction system. Examples of the compound convertible to its deprotonated product in the reaction system include a compound in which the deprotonated product is bonded to
25 other atom or atom group. Examples of the other atom or atom group bonded to the deprotonated product include various kinds of monovalent cations (such as Na⁺, K⁺ or

the like).

Among the above illustrated examples, the compound wherein A is an organic group having a nucleophilic oxygen and a carbon atom bonded to each other is 5 particularly preferable, and the following types (i) to (iv) oxygen nucleophilic agents are particularly preferable.

(i) Alcohols expressed by RO-H or RO⁻ (wherein R is an alkyl group which may have a substituent and may have 10 a double bond or a triple bond in a carbon chain) or their deprotonated products.

(ii) Hydroxy aryls expressed by ArO-H or ArO⁻ (wherein Ar is an aryl group which may have a substituent and may contain a hetero atom such as nitrogen, oxygen, 15 phosphorus or sulfur) or their deprotonated products.

(iii) Aliphatic carboxylic acids expressed by R'COO-H or R'COO⁻ (wherein R' is a hydrogen atom or an alkyl group which may have a substituent and may have a double bond or a triple bond in a carbon chain).

20 (iv) Aromatic carboxylic acids expressed by Ar'COO-H or Ar'COO⁻ (wherein Ar' is an aryl group which may have a substituent and may have a hetero atom such as nitrogen, oxygen, phosphorus or sulfur) or their deprotonated products.

25 Examples of the type (i) oxygen nucleophilic agent include a saturated or unsaturated alcohol and their substituent-containing products, and a saturated or

unsaturated diol, a multi-substituted alcohol or their substituent-containing products.

Examples of the saturated or unsaturated alcohol and their substituent-containing products include methyl
5 alcohol, ethyl alcohol, n-propyl alcohol, i-propyl alcohol, n-butyl alcohol, 2-ethylhexanol, n-octanol, allyl alcohol, crotyl alcohol, benzyl alcohol, 1-bromo-2-propanol, 2-methylcyclopentanol, 2-phenylethanol, neopentyl alcohol, 4-cyclohexenol, cholesterol and the
10 like. Examples of the saturated or unsaturated diol, the multi-substituted alcohol or their substituent-containing products include 1,2-ethane diol, 1,3-propane diol, 1,4-buthane diol, 2-butene-1,4-diol, 2-chloro-1,3-propane diol, 1,2-cyclopentane diol, glycerin, pentaerythritol
15 and the like.

Among the type (i) oxygen nucleophilic agents, a saturated alcohol or a saturated diol is preferable, examples of which include methyl alcohol, ethyl alcohol, n-propyl alcohol, i-propyl alcohol, n-butyl alcohol, 2-ethylhexanol, n-octanol and a C₁-C₁₀ diol such as 1,2-ethanediol, 1,3-propane diol or 1,4-buthane diol.

Examples of the type (ii) oxygen nucleophilic agents include monohydroxy aryl and their substituent-containing products, and di- or polyhydroxy aryl and their substituent-containing products. Examples of the monohydroxy aryl and their substituent-containing products include phenol, cresol, 4-nitrophenol, 2-

fluorophenol, 2,4-di-t-butylphenol, 2,4-di-t-butyl-6-methylphenol, 1-naphthol, 2-naphthol, 3-t-butyl-2-naphthol or the like. Examples of the di- or polyhydroxy aryl and their substituent-containing products include
5 catechol, resorcinol, hydroquinone, 2,4-dihydroxyphenyl ethyl ketone, 4-n-hexyl resorcinol, 1,8-dihydroxy naphthalene, 1,2-dihydroxy naphthalene, 1-methyl-2,3-dihydroxy naphthalene, 1,2,4-benzene triol or the like.

Among the type (ii) oxygen nucleophilic agents,
10 monohydroxy aryl or dihydroxy aryl is preferable, examples of which include phenol, 1-naphthol, 2-naphthol, catechol, resorcinol, hydroquinone or 2,6-dihydroxy naphthalene.

Examples of the type (iii) oxygen nucleophilic agents include a saturated aliphatic carboxylic acid and their substituent-containing products, an unsaturated aliphatic carboxylic acid and their substituent-containing products, and aliphatic dicarboxylic acids and their substituent-containing products, and the like.
15 Examples of the saturated aliphatic carboxylic acid and their substituent-containing products include acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, lauric acid, cyclohexane carboxylic acid, α -methyl butyric acid, γ -chloro- α -methyl valeic acid, α -hydroxy propionic acid, γ -phenyl butyric acid, and the like.
20 Examples of the unsaturated aliphatic carboxylic acid and their substituent-containing products include acrylic

acid, oleic acid, linolic acid, linolenic acid, 2-cyclohexene carboxylic acid, 4-methoxy-2-butenoic acid, methacrylic acid, and the like. Examples of the aliphatic dicarboxylic acid and their substituent-containing products include oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, and the like.

Among the type (iii) oxygen nucleophilic agents, a saturated aliphatic carboxylic acid or a saturated aliphatic dicarboxylic acid is preferable, examples of which include a C₁-C₂₀ acid such as acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, and the like.

Examples of the type (iv) oxygen nucleophilic agents include an aromatic carboxylic acid and their substituent-containing products, and an aromatic di- or polycarboxylic acid and their substituent-containing products. Examples of the aromatic carboxylic acid and their substituent-containing products include benzoic acid, 3-cyanobenzoic acid, 2-bromobenzoic acid, 2,3-dimethoxybenzoic acid, 4-phenoxybenzoic acid, p-nitrobenzoic acid, m-toluic acid, o-methoxybenzoic acid, phthalic acid monomethyl ester, terephthalic acid monoethyl ester, naphthalene-1-carboxylic acid, 1-methylnaphthalene-2-carboxylic acid, 2-ethoxynaphthalene-

1-carboxylic acid, 1-hydroxynaphthalene-2-carboxylic acid, 1-bromonaphthalene-2-carboxylic acid, anthracene-9-carboxylic acid, phenanthrene-4-carboxylic acid, picolinic acid, nicotinic acid, isonicotinic acid, 2-methoxythionicotinic acid, 6-chloronicotinic acid, isoquinoline-1-carboxylic acid, quinoline-3-carboxylic acid, quinoline-4-carboxylic acid, 4-methoxyquinoline-2-carboxylic acid, and the like. Examples of the aromatic di- or polycarboxylic acid and their substituent-containing products include phthalic acid, isophthalic acid, terephthalic acid, benzene-1,2,4-tricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid, naphthalene-1,4-dicarboxylic acid, naphthalene-1,8-dicarboxylic acid, naphthalene-2,3-dicarboxylic acid, naphthalene-2,6-dicarboxylic acid, naphthalene-1,4,5,8-tetracarboxylic acid, and the like.

Among the type (iv) oxygen nucleophilic agents, an aromatic carboxylic acid or dicarboxylic acid is preferable, examples of which include benzoic acid, naphthalene-2,6-dicarboxylic acid, phthalic acid, isophthalic acid or terephthalic acid.

Hereinafter, a catalyst used in the production method of the present invention is explained in details. The catalyst used in the present invention contains at least one transition metal compound and a monodentate coordinated phosphite compound.

The transition metal compound used in the present

invention is at least one kind of compound containing a transition metal selected from the group consisting of transition metals belonging to Group 8 to Group 10 of the Periodic Table (according to IUPAC Inorganic Chemistry Nomenclature, Revised Edition, 1998). Examples of the transition metal compound include an iron compound, a ruthenium compound, an osmium compound, a cobalt compound, a rhodium compound, an iridium compound, a nickel compound, a palladium compound and a platinum compound, and among them, a ruthenium compound, a rhodium compound, an iridium compound, a nickel compound, a palladium compound and a platinum compound are preferable, and a nickel compound, a palladium compound and a platinum compound are more preferable, and a palladium compound is particularly preferable. Kinds of these compounds are optional, examples of which include compounds of the above-mentioned transition metals such as an acetyl acetonate compound, a halide, a sulfate, a nitrate, an organic salt, an inorganic salt, an alkene-coordinated compound, an amine-coordinated compound, a pyridine-coordinated compound, a carbon monoxide-coordinated compound, a phosphine-coordinated compound, a phosphite-coordinated compound or the like.

Examples of the above transition metal compounds are illustrated below. Examples of the iron compound include Fe(OAc)_2 , Fe(acac)_3 , FeCl_2 , $\text{Fe(NO}_3)_3$ or the like. Examples of the ruthenium compound include RuCl_3 , Ru(OAc)_3 ,

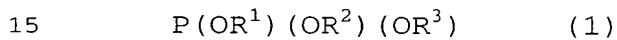
Ru(acac)₃, RuCl₂(PPh₃)₃ or the like. Examples of the osmium compound include OsCl₃, Os(OAc)₃ or the like. Examples of the cobalt compound include Co(OAc)₂, Co(acac)₂, CoBr₂, Co(NO₃)₂ or the like. Examples of the 5 rhodium compound include RhCl₃, Rh(OAc)₃, [Rh(OAc)₂]₂, Rh(acac)(CO)₂, [Rh(OAc)(cod)]₂, [RhCl(cod)]₂ or the like. Examples of the iridium compound include IrCl₃, Ir(OAc)₃, [IrCl(cod)]₂ or the like. Examples of the nickel compound include NiCl₂, NiBr₂, Ni(NO₃)₂, NiSO₄, Ni(cod)₂, 10 NiCl₂(PPh₃)₃ or the like. Examples of the palladium compound include Pd(0), PdCl₂, PdBr₂, PdCl₂(cod), PdCl₂(PPh₃)₂, Pd(PPh₃)₄, Pd₂(dba)₃, K₂PdCl₄, K₂PdCl₆, PdCl₂(PhCN)₂, PdCl₂(CH₃CN)₂, Pd(dba)₂, Pd(NO₃)₂, Pd(OAc)₂, Pd(CF₃COO)₂, PdSO₄, Pd(acac)₂, other carboxylate 15 compounds, an olefin-containing compound, an organic phosphine-containing compound such as Pd(PPh₃)₄, allyl palladium chloride dimer, or the like. Examples of the platinum compound include Pt(acac)₂, PtCl₂(cod), PtCl₂(CH₃CN)₂, PtCl₂(PhCN)₂, Pt(PPh₃)₄, K₂PtCl₄, Na₂PtCl₆, 20 H₂PtCl₆ or the like. In the above illustrations, "cod" means "1,5-cyclooctadiene", "dba" means "dibenzylideneacetone", "acac" means "acetylacetone", and "Ac" means "acetyl group".

Kinds of the transition metal compounds are not 25 specially limited, and may be a monomer, a dimer and/or a polymer so long as they are an active metal complex.

An amount of the transition metal compound used in

the present invention is not specially limited, but in view of a catalytic activity and economic conditions, it is preferable to use the transition metal compound in an amount of generally at least 1×10^{-8} (0.01 mol ppm) mol equivalent, preferably at least 1×10^{-7} (0.1 mol ppm) mol equivalent, more preferably at least 1×10^{-6} (1 mol ppm) mol equivalent, and generally at most 1 mol equivalent, preferably at most 0.001 mol equivalent, more preferably at most 0.0001 mol equivalent, to the amount of an allyl compound used as a reaction starting material.

The monodentate coordinated phosphite compound used in the present invention is a trialkyl type phosphite compound having a structure expressed by the following formula (1).



In the above formula (1), R^1 , R^2 and R^3 are respectively independently an alkyl group which may have a substituent. The alkyl group may be chain-like or cyclic, and the chain-like alkyl group may be linear chain-like or branched chain-like. Also, the carbon chain of the alkyl group may have at least one carbon-carbon double bond or triple bond. Kinds of a substituent of the above alkyl group are not specially limited so long as they do not adversely affect the reaction system, but examples of the substituent include a halogen atom, a nitro group, a cyano group, an amino group, a hydroxyl group, an acyl group, an acyloxy group,

a formyl group, an aryl group, an alkoxy group, an aryloxy group or the like.

Also, at least two optional groups among R¹, R² and R³ may be bonded to each other to form at least one cyclic structure. The number of rings is not specially limited, but is usually 0 to 3, preferably 0 to 2, more preferably 0 or 1. When a plurality of rings are present, a part of these rings may be jointly owned to form a condensed ring structure. Also, the number of atoms forming each ring is not specially limited, but is usually 3 to 10-membered ring, preferably 4 to 9-membered ring, more preferably 5 to 7-membered ring.

Carbon numbers of R¹, R² and R³ are respectively independently 1 to 20, preferably 1 to 15, more preferably 1 to 10. When at least two groups of R¹, R² and R³ are bonded to form a cyclic structure, their carbon number is usually 1 to 40×p, preferably 1 to 30×p, more preferably 1 to 20×p, when p is a number of groups participating in the formation of the cyclic structure.

Examples of R¹, R² and R³ are illustrated below. Examples of a linear or branched chain-like alkyl group which may have a substituent, include a methyl group, an ethyl group, a n-propyl group, an i-propyl group, a n-butyl group, an i-butyl group, a sec-butyl group, a t-butyl group, a pentyl group, a neopentyl group, a hexyl group, an octyl group, a 2-ethylhexyl group, a decyl group, a 2-chloroethyl group, a benzyl group, a 2,2,2-

trifluoroethyl group, a 3-dimethylaminopropyl group, a 1,1,1,3,3-hexafluoro-2-propyl group, a 5-cyanopentyl group, a 2-hydroxyethyl group, a 2-methoxyethyl group, a 3-(4-nitrophenyl)propyl group, and the like. Examples of 5 a cycloalkyl group include a cyclopentyl group, a cyclohexyl group, a 4-methylcyclohexyl group, a cycloheptyl group, a 2,3-diethylcyclohexyl group, a 4-ethoxydicyclohexyl group, a 3,5-dibromocyclohexyl group, and the like.

10 Examples of a chain-like or cyclic alkyl group having a double bond or a triple bond include an allyl group, a 2-butenyl group, a geranyl group, a 5-chloro-3-pentenyl group, a 2-propynyl group, a 2-butynyl group, and the like. Example of a chain-like or cyclic alkyl 15 group capable of forming a cyclic structure include a 1,1-diethylmethylen group, a 1,2-ethylene group, a 1,3-propylene group, a 1,3-dimethyl-1,3-propylene group, a 1,4-butylene group, a propane-1,1,1-trimethylene group, a 2-hydroxyethane-1,1,1-trimethylene group, a 3-20 hydroxypropane-1,1,1-triethylene group, and the like.

Among the above illustrated R¹, R² and R³ groups, a branched chain-like alkyl group or a cycloalkyl group is preferable.

Examples of the branched chain-like alkyl group 25 include an i-propyl group, a t-butyl group, a neopentyl group, a 2-ethylhexyl group, an isononyl group, an isodecyl group, a 4,4-dimethyl-1-pentyl group, and the

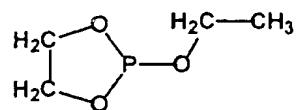
like.

Examples of the cycloalkyl group include a group having a carbon number of from 1 to 15 such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl 5 group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group and the like.

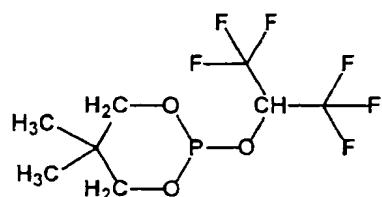
Further, among the above illustrated groups, particularly preferable examples include a group having a branched chain at the position of a carbon atom bonded to 10 an oxygen atom like a secondary alkyl group or a tertiary alkyl group. Examples of the secondary alkyl group or the tertiary alkyl group include an i-propyl group, a t-butyl group, a 1,1-dimethylpropyl group, a pentane-3-yl group, a heptane-3-yl group, a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, and the like.

Examples of the above-mentioned monodentate coordinated phosphite compound include trimethyl 20 phosphite, triethyl phosphite, tripropyl phosphite, tri-i-propyl phosphite, triallyl phosphite, tri-n-butyl phosphite, trioctadecyl phosphite, ethyldi-t-butyl phosphite, 2-ethylhexyldiethyl phosphite, diethylmethyl phosphite, dibenzyl-i-propyl phosphite, diisodecylallyl phosphite, tris(3-methoxypropyl) phosphite, tris(2-but enyl) phosphite, tris(2,2,2-trifluoroethyl) phosphite, tris(3-chloropropyl) phosphite, tricyclohexyl phosphite,

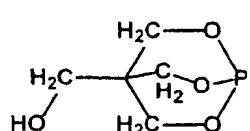
diisooctyl-2,3-dibromo-1-propyl phosphite,
trimethylolpropane phosphite, and compounds having the
following structural formulae (L-1) to (L-10).



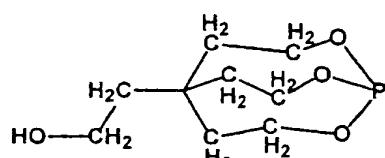
(L-1)



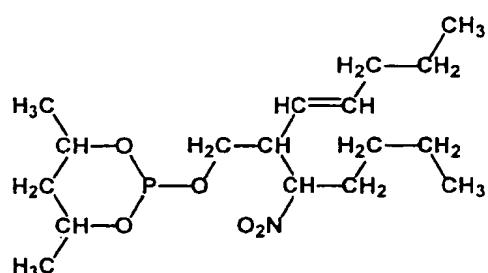
(L-2)



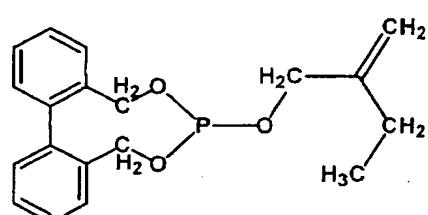
(L-3)



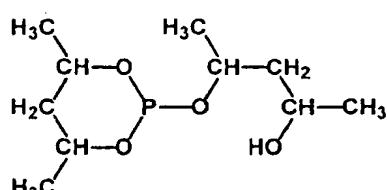
(L-4)



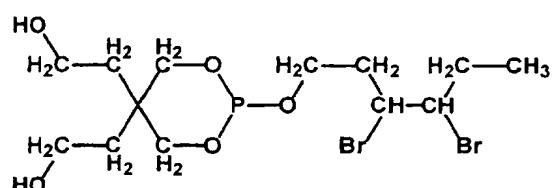
(L-5)



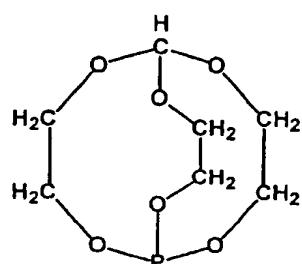
(L-6)



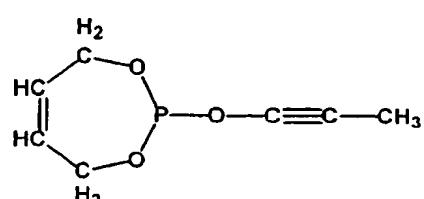
(L-7)



(L-8)



(L-9)



(L-10)

Among the above illustrated compounds, preferable examples include tri-i-propyl phosphite, ethyldi-t-butyl phosphite, 2-ethylhexyldiethyl phosphite, dibenzyl-i-propyl phosphite, diisodecylallyl phosphite,

5 tricyclohexyl phosphite, diisoctyl-2,3-dibromo-1-propyl phosphite, t-butyldiallyl phosphite, isoocetylbenzyl phosphite, di(3-chloropropyl)neopentyl phosphite, cyclopropylbis(2-butenyl) phosphite, diethyl-i-propyl phosphite, dimethyl-t-butyl phosphite, cyclohexyldimethyl phosphite, trineopentyl phosphite, diisoctylneopentyl phosphite, dicyclohexylisobutyl phosphite, and the above-mentioned compounds having the structural formulae (L-2), (L-5), (L-6) and (L-7).

Further, particularly preferable examples of the monodentate coordinated phosphite compound include compounds wherein R¹, R² and R³ are respectively independently a C₁-C₁₀ secondary alkyl or tertiary alkyl group. The examples include tri-i-propyl phosphite, ethyldi-t-butyl phosphite, dibenzyl-i-propyl phosphite, di-i-propyl-t-butyl phosphite, tri-t-butyl phosphite, tricyclohexyl phosphite, tricycloheptyl phosphite, dicyclohexyl-t-butyl phosphite, i-propyl-t-butyl-1,1-dimethylpropyl phosphite, and the like. Among them, tri-i-propyl phosphite is most preferable.

25 The monodentate coordinated phosphite compound is used in an amount of a mol ratio of usually at least 0.1, preferably at least 0.5, more preferably at least 1.0,

and usually at most 10,000, preferably at most 500, more preferably at most 100, to the above-mentioned transition metal compound.

Examples of a catalyst having a particularly
5 preferable activity include a combination of a palladium compound and a monodentate coordinated phosphite wherein at least one of R¹, R² and R³ is a C₁-C₁₅ branched chain-like alkyl or cycloalkyl group.

The above transition metal compound and the
10 monodentate coordinated phosphite compound may be added to the reaction system respectively alone, or may be previously complexed to be used. Alternatively, the above monodentate coordinated phosphite compound may be bonded to some insoluble resin carriers, and the above
15 transition metal compound may be carried thereon to form an insoluble solid catalyst to be used for the reaction. Further, only one kind of the monodentate coordinated phosphite compound may be used for the reaction, or an optional combination of at least two kinds of the
20 monodentate coordinated phosphite compounds may be used for the reaction.

By reacting an allyl starting material compound and an oxygen nucleophilic agent different therefrom in the presence of a catalyst comprising the above explained
25 transition metal compound and trialkyl type monodentate coordinated phosphite compound, a new allyl compound (such as ether compounds or ester compounds) can be

efficiently produced.

The reaction of the production method of the present invention is usually carried out in liquid phase. The reaction can be carried out either in the presence or
5 absence of a solvent. When using a solvent, any optional solvent is usable so long as it dissolves the catalyst and the starting material compound and does not adversely affect the catalyst activity, and the kind of the solvent is not specially limited. Preferable examples of the
10 solvent include carboxylic acids such as acetic acid, propionic acid or butyric acid, alcohols such as methanol, n-butanol or 2-ethylhexanol, ethers such as diglyme, diphenyl ether, dibenzyl ether, diallyl ether, tetrahydrofuran (THF) or dioxane, amides such as N-
15 methyl-2-pyrrolidone, dimethylformamide or dimethylacetamide, ketones such as cyclohexanone, esters such as butyl acetate, γ -butyrolactone or di(n-octyl) phthalate, aromatic hydrocarbons such as toluene, xylene or dodecylbenzene, aliphatic hydrocarbons such as
20 pentane, hexane, heptane or octane, a high boiling point material formed as a by-product in the allylation reaction system, and an allyl compound as a starting material, an allyl compound as a product, a compound derived from an eliminated group of a starting material
25 allyl compound and the like. An amount of these solvents is not specially limited, but is usually at least 0.1 weight time, preferably at least 0.2 weight time, and

usually at most 20 weight times, preferably at most 10 weight times, to a total amount of the allyl compound used as the starting material.

The actual reaction may be carried out by employing
5 various reaction systems. For example, the reaction can be carried out in any of continuous system, semi-continuous system or batch wise system by using a stirring type completely mixing reactor, a plug flow type reactor, a solid bed type reactor, a suspension bed type
10 reactor or the like.

When actually carrying out the reaction, reaction conditions may be optionally selected depending on a reaction substrate or a product. For example, when employing a stirring type completely mixing reactor, the
15 reaction is carried out by a process comprising adding a catalyst solution prepared in a catalyst-preparing tank to a mixture solution of an allyl starting material compound, an oxygen nucleophilic agent and an optionally a solvent, introducing the resultant mixture into the
20 reactor continuously or semi-continuously, retaining the reaction mixture at a reaction temperature with stirring to proceed the allylation reaction of the oxygen nucleophilic agent, and withdrawing a part of the reaction solution continuously or semi-continuously from
25 the reactor. Also, when employing a plug flow type reactor, the reaction is carried out by passing the reaction solution containing the above starting materials

and the catalyst through a tubular reactor maintained at a certain reaction temperature. This system is suitable for achieving a high conversion of the starting materials. Further, when employing an insoluble solid catalyst having a catalyst carried thereon, it is suitable to use a solid bed reaction system wherein the reaction is carried out by passing a solution containing starting materials through the reactor having the catalyst loaded, or it is possible to use a suspension bed reaction system wherein the reaction is carried out by stirring and mixing a solution containing starting materials and a particulate insoluble catalyst in a reactor and maintaining the reaction solution in suspension state.

The reaction temperature is not specially limited so long as it is a temperature at which the catalytic reaction proceeds, but when using a noble metal compound such as palladium, the reaction temperature should not be too high. If the reaction temperature is too high, there is a risk that metallization occurs and an effective catalyst concentration is reduced. Also, if the reaction temperature is too high, there is a risk that the phosphite compound is decomposed. Accordingly, a suitable reaction temperature is usually at least 0°C, preferably at least 20°C, more preferably at least 50°C, and usually at most 180°C, preferably at most 160°C, and more preferably at most 150°C.

The atmosphere in a reactor is preferably filled with a gas inert to the reaction system such as argon or nitrogen, in addition to vapors derived from a solvent, a starting material compound, a reaction product, a 5 reaction by-product, a decomposed material of catalyst and the like. Particularly, it is necessary to pay a special attention so that the atmosphere should not be mixed with oxygen for example by air leakage. If the atmosphere is contaminated with oxygen, the catalyst is 10 degraded and the phosphite compound is decomposed by oxidation. Thus, it is quite necessary to avoid the contamination of the atmosphere with oxygen.

The retention time of the reaction solution in the reactor, i.e. the reaction time, is varied depending on 15 an aimed conversion value of the starting material, but it is necessary to prolong the reaction time if a higher conversion is desired under a constant catalyst concentration. On the other hand, if it is desired to reduce the reaction time by maintaining the high 20 conversion, it is necessary to raise a catalyst activity by raising a catalyst concentration, increasing a catalyst amount or raising the reaction temperature. However, in order to avoid degradation of the catalyst or 25 a side reaction by heat history, it is preferable not to employ unnecessarily long reaction time or high temperature.

In this case, it is preferable for improving a

reaction activity to have a phosphonium compound and/or an ammonium compound present in the reaction system.

• Phosphonium compound

A phosphonium compound is not specially limited,
5 provided that it is stable under reaction conditions and is solved in the reaction system and does not poison the catalyst (examples of a compound poisoning a catalyst include a compound containing a conjugated diene, a compound oxidizing or decomposing a phosphite compound
10 such as a peroxide, and the like). In view of its solubility in the reaction system, the phosphonium compound has a molecular weight of usually at most 3,000, preferably at most 2,000, more preferably at most 1,500, and usually at least 40, preferably at least 70, more
15 preferably at least 100.

Among them, a phosphonium compound having a structure expressed by the following formula (2) is preferable.



20 In the above formula (2), X^1 to X^4 are respectively independently a hydrogen atom, a halogen atom, a hydroxyl group, an amino group, a chain-like or cyclic alkyl group, an aryl group (in the present specification, "aryl group" includes a heterocyclic compound forming an aromatic 6π electron cloud at the upper and lower parts of the ring), an alkoxy group, an aryloxy group, an alkylthio group or an arylthio group. The above

illustrated groups may further have a substituent. The substituent is not specially limited so long as it does not adversely affect the reaction system, and preferable examples of the substituent include a halogen atom, a 5 hydroxyl group, an amino group, a chain-like or cyclic alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group or an arylthio group. When the above illustrated unsubstituted or substituted groups contain a carbon chain, the carbon chain may have at 10 least one carbon-carbon double bond or triple bond.

The carbon number of X^1 to X^4 are respectively independently usually at most 40, preferably at most 30, more preferably at most 20. At least two optional groups of X^1 to X^4 may be bonded to each other to form at least 15 one cyclic structure. The number of cycles is not specially limited, but is usually 0 to 3, preferably 0 to 2, more preferably 0 or 1. When at least two groups of X^1 to X^4 are bonded to form a cyclic structure, its carbon number is usually at most $40 \times p$, preferably at most 20 $30 \times p$, more preferably at most $20 \times p$, wherein p is the number of groups participating in the formation of a 25 cyclic structure. Also, the number of atoms forming each ring is not specially limited, but is usually 3 to 10-membered ring, preferably 4 to 9-membered ring, more preferably from 5 to 7-membered ring. When a plurality of rings are present, these rings may be partly jointly owned to form a condensed ring structure.

Among the above illustrated groups, preferable examples of X^1 to X^4 are respectively independently a hydrogen atom, a substituted or unsubstituted chain-like or cyclic alkyl group, an aryl group, an alkoxy group, an 5 arylalkoxy group or an aryloxy group, and more preferable examples include a substituted or unsubstituted chain-like or cyclic alkyl group or an aryl group (in this case also, at least two optional groups of the alkyl group or the aryl group of X^1 to X^4 may be bonded to form at least 10 one cyclic structure as mentioned above).

Particularly, at least one group of X^1 to X^4 is preferably a group capable of dispersing +1 valent charge on the phosphorus atom of a phosphonium compound by resonance effect. The phosphonium compound having such a 15 group can provide a counter cation for forming a loose ion pair. Examples of a group capable of providing such resonance stabilization of cation include a substituted or unsubstituted aryl or a vinyl group, typical example of which include a phenyl group, a 4-methoxyphenyl group, 20 4-t-butylphenyl group, a 2,4-di-t-butylphenyl group, a 2,4-di-t-butyl-6-methylphenyl group, a 2,5-dimethylphenyl group, a 2,4,6-trimethoxyphenyl group, a 1-naphthyl group, a 2-naphthyl group, a 1-methyl-2-naphthyl group, a vinyl group or a 1-butenyl group. Among them, when 25 taking a strength of effect of resonance stabilization or easy synthesis of a phosphonium compound into consideration, a substituted or unsubstituted aryl group

is particularly preferable.

Examples of the phosphonium compound usable in the present invention include hydroxytrimethoxyphosphonium, hydroxymethoxydimethylphosphonium,
5 chlorohydroxydicyclohexylphosphonium, bromotriethoxyphosphonium, trichloro-3-phenoxy-1-propenylphosphonium, dichlorohydroxyphenylphosphonium, tri(t-butoxy)cyclohexylphosphonium, fluorotris(4-methoxyphenyl)phosphonium, methyltri(phenoxy)phosphonium,
10 dimethylaminotris(4-ethylphenyl)phosphonium, tri(ethylthio)hydroxyphosphonium, diethoxyethylphenylthiophosphonium, trifluoromethyltris(dimethylamino)phosphonium, tetra(t-butyl)phosphonium, trimethyl-1-propynylphosphonium, and
15 the like.

Among them, in view of stability and solubility, preferable examples include phosphonium compounds having respectively independently a hydrogen atom, a substituted or unsubstituted chain-like or cyclic alkyl group, an aryl group, an alkoxy group, an arylalkoxy group, an aryloxy group or an alkylaryloxy group as X¹ to X⁴.
Typical examples of such phosphonium compounds include tetra(n-dodecyl)phosphonium, tetrakis(2-octenyl)phosphonium, cyclohexyltris(2-methyl-2-butenyl)phosphonium, methoxymethyldi(n-butyl)phosphonium, allyl-t-butylethylphenoxyphosphonium, 4-acetoxy-2-butenylphenylbis(2,4-di-t-butylphenoxy)phosphonium, t-

butoxy-3-bromo-1-naphthoxybis(4-nitrophenyl)phosphonium,
di(1-naphthoxy)-2,4-di-t-butyl-5-methylphenoxy-2-acetoxy-
3-butenylphosphonium, 2-butene-1,4-bis(tris(2-
methoxyphenoxy)phosphonium), tetrakis(2,4,6-
5 trimethoxyphenoxy)phosphonium, and the like.

Further, more preferable examples of a phosphonium compound include a compound having a chain-like or cyclic and substituted or unsubstituted alkyl or aryl group as X¹ to X⁴. These preferable examples include a phosphonium 10 compound having a structure wherein all of the four substituents X¹ to X⁴ of the phosphonium compound are bonded to a phosphorus atom by P-C bond. Examples of such a phosphonium compound include

tetramethylphosphonium, tetra(n-butyl)phosphonium,
15 tetra(methylol)phosphonium, 4-acetoxybutyldiethyl-2-methoxyethylphosphonium, neopentyltriphenylphosphonium, tetr phenylphosphonium, tetrakis(4-fluorofluorophenyl)phosphonium, 2-butenylbis(4-t-butylphenyl)-3-cyanopropylphosphonium,
20 methyltriphenylphosphonium, 4-methylcyclohexyltri(i-propyl)phosphonium, dimethylpentamethylenephosphonium, 4-acetoxy-2-butenyltriphenylphosphonium, 2-butenyl-1,4-bis(triphenylphosphonium), naphthalene-1,8-bis(trimethylphosphonium), biphenyl-2,2'-bis(diphenylmethylphosphonium), and the like. Also, the examples include all of a phosphonium compound having an allyl group derived from reaction of phosphine and an

allyl compound.

Particularly preferable examples include a phosphonium compound wherein at least one of X¹ to X⁴ is a group capable of dispersing +1 valent charge on a phosphorus atom by resonance effect, as mentioned above.

Examples of such a preferable phosphonium compound include trimethylphenylphosphonium, 4-acetoxy-2-butenyldicyclohexylphenylphosphonium, 2-butenyl-1,4-bis(dicyclohexylphenylphosphonium), triethyl-1-naphthylphosphonium, tri-n-butyl-1-methyl-2-naphthylphosphonium, diethylphosphinedrium, 4-acetoxy-2-butenyldiphenyl-i-propylphosphonium, 2-butenyl-1,4-bis(diphenyl-i-propylphosphonium), dimethylbis(2,4-dimethylphenyl)phosphonium, t-butyl-1-acetoxymethyl-2-propenylbis(2-naphthyl)phosphonium, diphenylisophosphinedrium, methyltriphenylphosphonium, 4-acetoxy-2-butenyltriphenylphosphonium, 2-butenyl-1,4-bis(triphenylphosphonium), 1-butene-3,4-bis(triphenylphosphonium), 1-acetoxymethyl-2-propenyltris(4-methoxydiphenyl)phosphonium, tetraphenylphosphonium, di(1-naphthyl)diphenylphosphonium, tetrakis(2-naphthyl)phosphonium, naphthalene-2,6-bis(triphenylphosphonium), and the like.

Further, in order to further weaken cationic property of phosphonium, it is preferable that such an aryl group has an electron donative substituent such as

an alkyl group or a methoxy group.

When the above-mentioned phosphonium compound is present in the reaction system of carrying out allylation reaction, an effect of improving a reactivity is achieved. In this case, any one kind of phosphonium compound may be used alone or several kinds of phosphonium compounds may be used by optionally combining and mixing.

A method for introducing the phosphonium compound into the reaction system is not specially limited, but there is a method of positively adding the phosphonium compound to the reaction system or a method of preparing the phosphonium compound in the reaction system. These methods are further explained hereinafter by referring to examples.

First, the method of positively adding the phosphonium compound to the reaction system is a method of feeding the phosphonium compound together with an allyl compound, a nucleophilic agent, a catalyst, a reaction medium and the like to a reactor, and the phosphonium compound may be a new phosphonium compound or a phosphonium compound recycled from the reaction process. In connection with this, it should be noted that since a commercially available phosphonium compound is generally charged with +1 valent charge per one phosphorus atom, it is in a form of salt with its corresponding counter anion, but the counter anion

corresponding to phosphonium is preferably a nucleophilic agent reactive with an allyl starting material compound in the reaction system. If the counter anion is not a nucleophilic agent but a phosphonium compound in a form 5 of salt with other counter anion is added, it is desired that the other counter anion does not poison a catalyst and is decomposed by reacting with an allyl compound in the reaction system so that a nucleophilic agent becomes newly a counter anion. Generally known examples of a 10 counter anion of a commercially available phosphonium compound include a halogen atom ion such as chloride, bromide or iodide, and hexafluorophosphate, hexachlorophosphate, hydrogen sulfate, tetrachloroborate, trifluoromethanesulfonate, perchlorate or the like.

15 Among these examples, it is generally considered that there is a high possibility that a halide ion poisons a transition metal catalyst. When using such a halide phosphonium compound, it is preferable to previously remove a halide ion by anion exchange reaction. In this 20 case, it is more preferable to make a nucleophilic agent using a new counter anion in the allylation reaction.

On the other hand, the method of preparing a phosphonium compound in the reaction system includes a 25 method of adding a trivalent phosphorus compound as a starting material for phosphonium. This method uses such a reaction as described in the J. Am. Chem. Soc., 1992, 114, p6858, and this reaction comprises nucleophilically

attacking a terminal allyl carbon of a π -allyl complex of transition metal by a trivalent phosphorus compound to form a phosphonium compound having an allyl group newly bonded. When carrying out such a process, it should be
5 noted that a ligand coordinated to a transition metal compound is eliminated and a catalyst activity is lowered when a coordination power of a trivalent phosphorus compound added as a starting material for phosphonium to a transition metal compound is too high. In such a case,
10 it is necessary to previously convert into a phosphonium compound at the outside of the system before feeding or to wait for slowly converting into a phosphonium compound during carrying out the process.

In view of economic conditions, it is advantageous
15 to use the above phosphonium compound in a small amount. Thus, the phosphonium compound is used to a metal compound as an allylation catalyst (fully described above) at a mol ratio of usually at least 0.1, preferably at least 1, more preferably at least 5, further
20 preferably at least 10, most preferably at least 15, and usually at most 10,000, preferably at most 5,000, more preferably at most 1,000, most preferably at most 500.

• Ammonium compound

An ammonium compound usable in the present invention
25 basically has a structure having four substituents bonded to nitrogen. Usually, the usable ammonium compound is not specially limited so long as it is stable under the

reaction conditions and soluble in the reaction system and does not poison a catalyst (examples of a compound poisoning the catalyst include a compound containing a conjugated diene, a compound oxidizing and decomposing a phosphite compound such as a compound containing peroxide, and the like). In view of its solubility in the reaction system, the ammonium compound has a molecular weight usually at most 3,000, preferably at most 2,000, more preferably at most 1,000, and usually at least 20, preferably at least 40, more preferably at least 60.

Among them, an ammonium compound having a structure expressed by the following formula (3) is preferable.



In the above formula (3), X^1 to X^4 are respectively independently a hydrogen atom, a halogen atom, a hydroxyl group, an amino group, a chain-like or cyclic alkyl group, an aryl group (in the present specification, "aryl group" includes a heterocyclic compound forming an aromatic $6n$ electron cloud at the upper and lower parts of the ring), an alkoxy group, an aryloxy group, an alkylthio group or an arylthio group. The above illustrated groups may further have a substituent. The substituent is not specially limited so long as it does not adversely affect the reaction system, and preferable examples of the substituent include a halogen atom, a hydroxyl group, an amino group, a chain-like or cyclic

alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group or an arylthio group. When the above illustrated unsubstituted or substituted groups contain a carbon chain, the carbon chain may have at 5 least one carbon-carbon double bond or triple bond.

The carbon number of X^1 to X^4 are respectively independently usually at most 40, preferably at most 30, more preferably at most 20. At least two optional groups of X^1 to X^4 may be bonded to each other to form at least 10 one cyclic structure. The number of cycles is not specially limited, but is usually 0 to 3, preferably 0 to 2, more preferably 0 or 1. When at least two groups of X^1 to X^4 are bonded to form a cyclic structure, its carbon number is usually at most $40 \times p$, preferably at most 15 $30 \times p$, more preferably at most $20 \times p$, wherein p is the number of groups participating in the formation of a cyclic structure. Also, the number of atoms forming each ring is not specially limited, but is usually 3 to 10-membered ring, preferably 4 to 9-membered ring, more 20 preferably from 5 to 7-membered ring. When a plurality of rings are present, these rings may be partly jointly owned to form a condensed ring structure.

Among the above illustrated groups, preferable examples of X^1 to X^4 are respectively independently a 25 hydrogen atom, a substituted or unsubstituted chain-like or cyclic alkyl group, an aryl group, an alkoxy group, an arylalkoxy group, an aryloxy group or an alkylaryloxy

group, and more preferable examples include a substituted or unsubstituted chain-like or cyclic alkyl group or an aryl group (in this case also, at least two optional groups of the alkyl group or the aryl group of X^1 to X^4 5 may be bonded to form at least one cyclic structure).

Further, the ammonium compound expressed by the above formula (3) include a compound having an N=C double bond such as N-substituted pyridine, N-substituted oxazolium, N-substituted thiazolium, and the like. Still 10 further, the above ammonium compound includes mono- or polyammonium compounds derived from polyamines such as bidentate chelate type diamines having an amino group as a substituent.

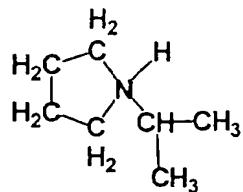
Examples of the ammonium compound usable in the 15 present invention include trimethoxyammonium, methoxydimethyl ammonium, chlorohydroxydicyclohexyl ammonium, bromotriethyl ammonium, dimethylthiodiphenyl ammonium, tri(*t*-butyl)cyclohexyl ammonium, ethoxytris(4-methoxyphenyl) ammonium, methyltri(phenoxy) ammonium, 20 dimethoxyacetyl ammonium, tri(ethylthio)isopropyl ammonium, diethoxyethylphenylthio ammonium, tetra(*n*-butyl) ammonium, triethylhydro ammonium, trimethyl-1-propynyl ammonium, N-*t*-butyl-5-methyloxazolium, 4-methoxypyridinium, N-phenylthiazolium, Et₂HN-CH₂-CH₂-NET₂, 25 Me₂HN-CH₂-CH₂-CH₂-NHMe₂, Me₂HN-CH₂-CH₂-NHMe₂, and the like. In the present specification, Me represents a methyl group and Et represents an ethyl group.

However, generally, compounds easily available and suitably usable in the present invention include the following two types of compounds.

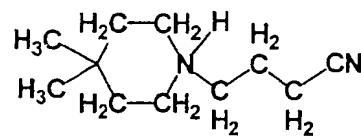
(i) Compounds wherein one of X^1 to X^4 is a hydrogen atom, and the other three groups are respectively independently a substituted or unsubstituted alkyl or aryl group (at least two optional groups of these alkyl or aryl groups may be bonded to each other to form at least one cyclic structure).

(ii) Compounds wherein all of X^1 to X^4 are respectively independently a substituted or unsubstituted alkyl or aryl group (at least two optional groups of these alkyl or aryl groups may be bonded to each other to form at least one cyclic structure).

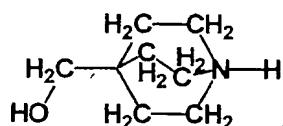
Examples of the above type (i) compound include triethyl ammonium, triisopropyl ammonium, tri-n-dodecyl ammonium, diethylisopropyl ammonium, ethyl-n-propyl-t-butyl ammonium, 3-chloro-1-propyldiphenyl ammonium, triallyl ammonium, geranyl bis(4-methoxyphenyl) ammonium, tris(2,4-dimethylphenyl) ammonium, 3-fluorophenyl-2-methylphenyl-2-naphthyl ammonium, tri(2-naphthyl) ammonium, pyridinium, 4-t-butyl ammonium, 4-cyanopyridinium, and compounds expressed by the following formulae (N-1) to (N-6).



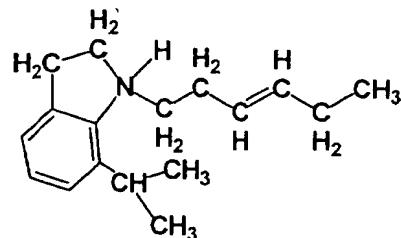
(N-1)



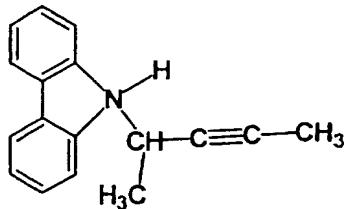
(N-2)



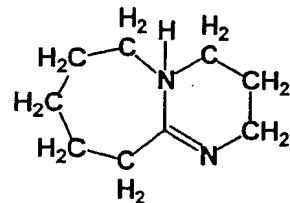
(N-3)



(N-4)



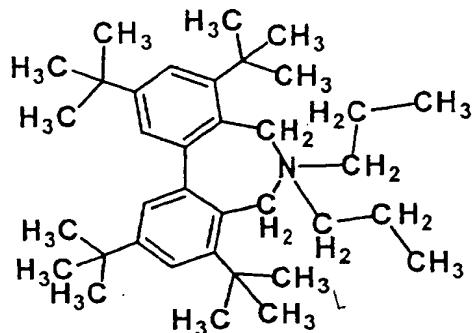
(N-5)



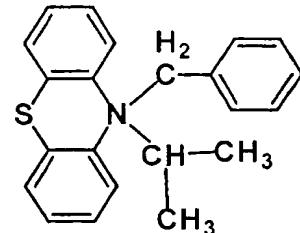
(N-6)

Examples of the above type (ii) compounds include tetramethyl ammonium, tetrabenzyl ammonium, tetraundecenyl ammonium, trimethylethyl ammonium, triallyl-3-pentynyl ammonium, triethylallyl ammonium, diphenylmethylethyl ammonium, trimethyl-2-but enyl ammonium, bis(4-methoxy-1-butyl)diethyl ammonium, di(1-naphthyl)diisopropyl ammonium, t-butylethylisopropyl-4-fluorophenyl ammonium, tris(4-ethylphenyl)-4-acetoxy-2-but enyl ammonium, and compounds expressed by the

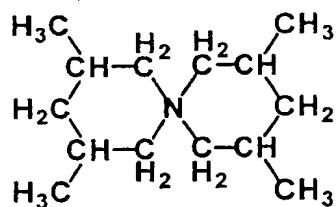
following formulae (N-7) to (N-12).



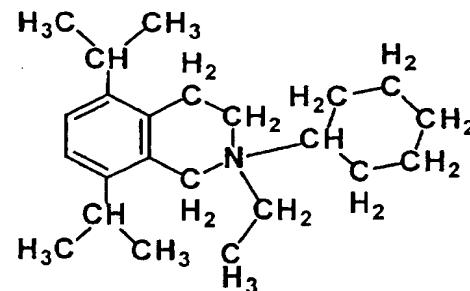
(N-7)



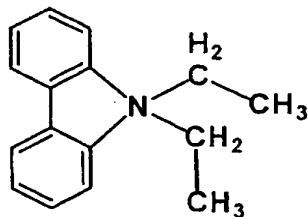
(N-8)



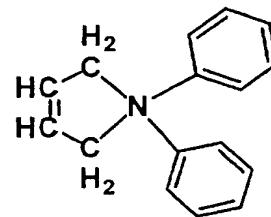
(N-9)



(N-10)



(N-11)



(N-12)

Among the above-mentioned type (i) and type (ii) compounds, an ammonium compound wherein X^1 to X^4 other than hydrogen are a substituted or unsubstituted alkyl or aryl group is preferable. Examples of such type (i)

ammonium compounds include tri-n-octyl ammonium, tris(6-t-butyl-2-naphthyl) ammonium, di-n-propylethylmethyl ammonium, n-propyl-n-butyl-n-pentyl ammonium, 2-chloroethyl-3-methoxypropyl-4-trimethylsilylbutyl ammonium, and the like, and examples of such type (ii) ammonium compounds include tetra-n-nonyl ammonium, tetraphenyl ammonium, diethyldiisopropyl ammonium, triethylbenzyl ammonium, methylethyl-n-propyl-n-butyl ammonium, methyl-t-butyldi(1-naphthyl) ammonium, 5-bromopentyldiethylmethyl ammonium, tris(2,5-dimethylphenyl)-n-octyl ammonium, and the like.

Among the above type (i) and type (ii) ammonium compounds, type (i) ammonium compounds are more preferable from an economical viewpoint since the type (i) ammonium compounds can be easily prepared by acid-base reaction of an acidic material such as acetic acid or phenol and original tertiary amine excluding coordinate-bonded proton. Particularly, type (i) ammonium compounds wherein all of three alkyl groups other than proton are the same are preferable since their production cost is cheap. Examples of such an ammonium compound include an ammonium compound wherein proton is coordinate-bonded to a trialkylamine having the same alkyl groups, such as triethyl ammonium, tri-n-propyl ammonium, triisopropyl ammonium, tri-n-butyl ammonium, tri-sec-butyl ammonium, tri-n-pentyl ammonium, tri-n-neopentyl ammonium, tri-i-octyl ammonium, tri-n-octyl

ammonium, tridecanyl ammonium, and the like. Further, an ammonium compound wherein proton is coordinate-bonded to 1,8-diazabicyclo[5.4.0]undecene-7 (DBU) is preferable.

The above-mentioned ammonium compounds achieve an
5 effect of improving a reactivity when they are present in
the reaction system of carrying out allylation reaction.
In this case, any one kind of ammonium compound may be
present alone, or a plurality of kinds of ammonium
compounds may be mixed in optional combination.

10 A method for introducing an ammonium compound into
the reaction system is not specially limited, but its
examples include a method of positively adding the
ammonium compound to the reaction system or a method of
preparing the ammonium compound in the reaction system.
15 These methods are further explained by giving concrete
examples hereinafter. First, the method of positively
adding the ammonium compound to the reaction system is a
method of feeding the ammonium compound together with an
allyl compound, a nucleophilic agent, a catalyst, a
20 reaction medium and the like into a reactor, and the
ammonium compound may be a new ammonium compound or may
be an ammonium compound recycled from the reaction
process. In this regard, it should be noted that since a
commercially available ammonium compound generally has +1
25 valent charge per one nitrogen, it takes a form of salt
with its corresponding counter anion, but it is
preferable that this counter anion corresponding to

ammonium is a nucleophilic agent to be reacted with an allyl starting material compound in the reaction system. If the counter anion is not a nucleophilic agent and an ammonium compound in a form of a salt with other counter 5 anion is added, it is desired that the other counter anion does not poison a catalyst and is decomposed by reaction with an allyl compound in the reaction system, and a nucleophilic agent newly becomes a counter anion. Generally known examples of a counter anion of a 10 commercially available ammonium compound include a halide ion such as chloride, bromide or iodide, and hexafluorophosphate, hexachlorophosphate, hydrogen sulfate, tetrachloroborate, trifluoromethane sulfonate, perchlorate and the like. Among them, it is generally 15 considered that there is a high possibility that the halide ion poisons a transition metal catalyst. When such a halogenated ammonium compound is used in the reaction, it is preferable to previously remove it by anionic change reaction or the like. In this case, it is 20 more desirable that a new counter anion is used as a nucleophilic agent to be used for allylation reaction.

On the other hand, examples of the method of preparing an ammonium compound in the reaction system include a method of adding an amine or pyridine compound 25 as a starting material for ammonium. In this method, these compounds showing a basic property causes acid-base reaction with a proton acidic site of a nucleophilic

agent in a reactor, and as this result, an ammonium or pyridinium compound having a structure having proton coordinate-bonded to a non-covalent electron pair on nitrogen. When carrying out such a process, it should be
5 noted that when a nucleophilic agent has a proton acidic site, this method can be satisfactorily carried out and achieves a substantial effect particularly in the reaction of an oxygen nucleophilic agent such as phenol or carboxylic acids and a carbon nucleophilic agent such
10 as malonic acid ester derivatives, but when a nucleophilic agent is a nitrogen nucleophilic agent such as amines, a substantial effect can not be achieved since amines are originally basic. Further, it should be noted that when an amine compound added as a starting material
15 for ammonium has an excessively high coordinative power to a transition metal compound, a ligand originally coordinated to a transition metal compound is eliminated and a catalyst activity is lowered. In such a case, it is necessary to previously convert an amine compound into
20 an ammonium compound at the outside of the system before feeding or to wait that an amine compound is gradually converted into an ammonium compound during carrying out the process.

It is advantageous from an economical viewpoint that
25 the above ammonium compound is used in a smaller amount. Thus, the ammonium compound is used in a mol ratio of usually at least 0.1, preferably at least 1, more

preferably at least 5, further preferably at least 10,
most preferably at least 15, and usually at most 10,000,
preferably at most 5,000, more preferably at most 1,000,
most preferably at most 500, to a metal compound as an
5 allylation reaction catalyst as fully illustrated above.

Also, many separating operations used in a conventional liquid catalyst recycling process can be employed for separating a catalyst and an allyl compound obtained in the reaction. Examples of the separating
10 operations include distillation operations such as simple distillation, vacuum distillation, thin film distillation, water vapor distillation or the like, and other separating operations such as gas-liquid separation, evaporation, gas stripping, gas absorption
15 and extraction. The separating operation of each component may be carried out respectively in an independent step, or separation of two or more components may be carried out at the same time in a single step. When a part of an allyl starting material compound or an
20 unreacted nucleophilic agent remains, they may be recovered by a separating method in the same manner as above and may be recycled into a reactor, which provides an economical advantage. Further, it is economically desirable to recycle the separated catalyst into the
25 reactor as it is or to recover the separated catalyst to be reactivated for reuse.

EXAMPLES

Hereinafter, the present invention is further fully illustrated by the following Examples, but should not be limited thereto.

5 EXAMPLES 1 to 2 and COMPARATIVE EXAMPLES 1 to 3

Allylphenyl ether synthesis reaction of the present invention was carried out by using allylmethyl carbonate as an allyl starting material compound and phenol as an oxygen nucleophilic agent.

10 A catalyst solution having a palladium concentration of 15.05 mmol/l was prepared by adding 0.0149 g (0.0151 mmol) of trisdibenzylideneacetone dipalladium having a palladium content of 21.5 wt% as a transition metal compound and triisopropyl phosphite (Example 1) or 15 triethyl phosphite (Example 2) in an amount of 8 equivalents (0.2408 mmol) to palladium as a trialkyl type monodentate coordinated phosphite compound to a container substituted with argon, adding 2.0 ml of tetrahydrofuran thereto and stirring the resultant mixture at room 20 temperature. Thereafter, in order to carry out the reaction, another container was substituted with argon, and 5.0 ml of a tetrahydrofuran solution containing 0.1720 g (1.481 mmol) of allylmethyl carbonate and 0.2707 g (2.877 mmol) of phenol was added into the container 25 under argon atmosphere. 20.0 μ l of the above prepared catalyst solution was added thereto by a microsyringe, and the resultant mixture was heated at 60°C to carry out

the reaction. After reacting for 30 minutes, the resultant solution composition was analyzed by gas chromatography to determine a yield of allylphenyl ether.

As Comparative Examples, the same procedure was
5 repeated by using conventionally used 1,4-bis(diphenylphosphino)butane (dppb) as a bidentate phosphine ligand (Comparative Example 1), triphenylphosphite ligand as a triaryl type monodentate coordinated phosphite ligand (Comparative Example 2) and
10 tris(2,4-di-t-butylphenyl) phosphite (Comparative Example 3). In the case of using dppb which is a bidentate ligand, it was added in an amount of 4 equivalents to palladium.

The results are shown in the following Table 1.

15

Table 1

	Ligand	Allylphenyl ether yield
Ex. 1	Triisopropyl phosphite	97%
Ex. 2	Triethyl phosphite	50%
Comp. Ex. 1	Dppb	4%
Comp. Ex. 2	Triphenyl phosphite	3%
Comp. Ex. 3	Tris(2,4-di-t-butylphenyl) phosphite	0%

EXAMPLE 3 and COMPARATIVE EXAMPLES 4 to 7

Allyloctyl ether synthesis reaction of the present
20 invention was carried out by using allyl acetate as an

allyl starting material compound and 1-octanol as an oxygen nucleophilic agent.

The reaction was carried out by adding 0.0048 g (0.0048 mmol) of trisdibenzylideneacetone dipalladium having a palladium content of 21.5 wt% as a transition metal compound and triisopropyl phosphite (0.0389 mmol) in an amount of 4 equivalents to palladium as a trialkyl type monodentate coordinated phosphite compound to a container substituted with argon, adding 0.943 g (9.420 mmol) of allyl acetate and 2.422 g (18.594 mmol) of 1-octanol under argon atmosphere thereto, and heating the resultant mixture at 100°C to carry out the reaction. After reacting for 60 minutes, the resultant solution composition was analyzed by gas chromatography to determine a yield of allyloctyl ether.

Also, as Comparative Examples, the same reaction procedure was repeated by using conventionally used 1,4-bis(diphenylphosphino)butane (dppb) as a bidentate phosphine ligand (Comparative Example 4), triphenyl phosphine as a monodentate phosphine ligand (Comparative Example 5), triphenyl phosphite ligand as a monodentate coordinated phosphite ligand (Comparative Example 6) and tris(2,4-di-t-butylphenyl) phosphite (Comparative Example 7). However, in the case of using dppb as a bidentate ligand, it was added in an amount of 2 equivalents to palladium.

The results are shown in the following Table 2.

Table 2

	Ligand	Allyloctyl ether yield
Ex. 3	Triisopropyl phosphite	38%
Comp. Ex. 4	Dppb	7%
Comp. Ex. 5	Triphenyl phosphine	7%
Comp. Ex. 6	Triphenyl phosphite	3%
Comp. Ex. 7	Tris(2,4-di-t-butylphenyl) phosphite	1%

EXAMPLE 4 and COMPARATIVE EXAMPLES 8 to 9

Allyl benzoate synthesis reaction of the present
5 invention was carried out by using allyl acetate as an
allyl starting material compound and benzoic acid as an
oxygen nucleophilic agent.

A catalyst solution having a palladium concentration
of 15.05 mmol/l was prepared by adding 0.0149 g (0.0151
10 mmol) of trisdibenzylideneacetone dipalladium having a
palladium content of 21.5 wt% as a transition metal
compound and triisopropyl phosphite (0.2409 mmol) in an
amount of 8 equivalents to palladium as a trialkyl type
monodentate coordinated phosphite compound to a container
15 substituted with argon, adding 2.0 ml of tetrahydrofuran
thereto, and stirring the resultant mixture at room
temperature. Thereafter, in order to carry out the
reaction, another container was substituted with argon,
and 4.0 ml of a tetrahydrofuran solution containing
20 0.3083 g (2.525 mmol) of benzoic acid and 0.1208 g (1.206

mmol) of allyl acetate was added thereto under argon atmosphere. 60.0 μ l of the above prepared catalyst solution was added thereto by a microsyringe, and the resultant mixture was heated at 60°C to carry out the reaction. After reacting for 30 minutes, the resultant solution composition was analyzed by gas chromatography to determine a yield of allyl benzoate.

Also, as Comparative Examples, the same reaction procedure was repeated by using conventionally used 1,4-bis(diphenylphosphino)butane (dppb) as a bidentate phosphine ligand (Comparative Example 8) and triphenyl phosphine ligand as a monodentate coordinated phosphine ligand (Comparative Example 9). However, in the case of using dppb as a bidentate ligand, it was added in an amount of 4 equivalents to palladium.

The results are shown in the following Table 3.

Table 3

	Ligand	Allyl benzoate yield
Ex. 4	Triisopropyl phosphite	60%
Comp. Ex. 8	Dppb	1%
Comp. Ex. 9	Triphenyl phosphite	21%

As evident from the above results, it is clear that the catalyst comprising the trialkyl type monodentate coordinated phosphite ligand of the present invention

provides a higher activity as compared with the catalyst comprising the bidentate phosphine type ligand, monodentate phosphine type ligand or triaryl type monodentate coordinated phosphite conventionally used.

5 According to the present invention, since a new catalyst system achieving a sufficiently high catalyst activity to an oxygen nucleophilic agent having a low reactivity is used for reacting an oxygen nucleophilic agent with an allyl starting material compound to produce
10 a new allyl compound, more various kinds of allyl compounds can be produced more efficiently as compared with the conventional catalyst system.

The entire disclosure of Japanese Patent Application No. 2002-251620 filed on August 29, 2002 including
15 specification, claims and summary is incorporated herein by reference in its entirety.